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Technical Notes

Continuous Single-Stage Organomagnesium Synthesis of a Mixture of Ethylethoxysilanes and Dimethylethylethoxysilane

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Abstract:

Simultaneous synthesis of ethylethoxysilanes and dimethylethylethoxysilane from a mixture of ethyl chloride, tetraethoxysilane, and dimethyldichlorosilane with magnesium (supply rate 75−100 g h^{-1}) was studied. Schemes of intermediate processes are proposed. Reactivity of dimethyldichlorosilane and diethyldichlorosilane relative to each other is evaluated. Various grades of magnesium are tested. To reduce the amount of regenerated solvent (toluene) its mixtures with oligodiethylsiloxanes are used. The mixture of ethyl-substituted silanes can be used in subsequent preparation of oligo-ethylsiloxane liquids modified with the terminal dimethylethylsiloxy groups, which are characterised by improved lubricating properties.

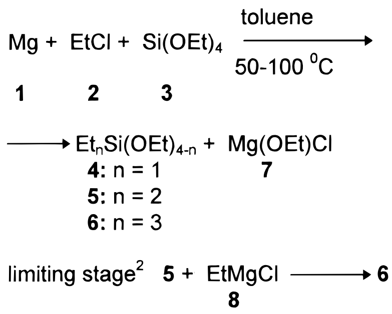
Introduction

A continuous process developed by us for the synthesis of ethylethoxysilanes (Scheme 1), which is used in production of oligoethylsiloxanes,[1,2] and for production of silicone intermediates (polyolefin catalysis),[2a,b]is performed with the excess of granulated magnesium[3] in a stirring column apparatus with a countercurrent mode relative to liquid reagents.

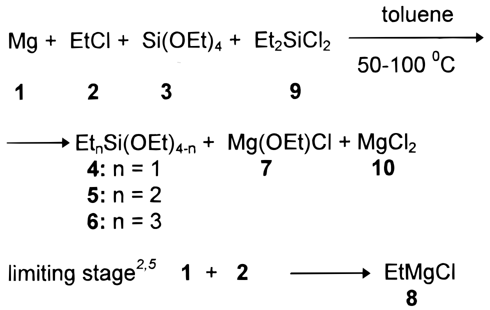
To improve this process, we proposed using of a mixture of tetraethoxysilane **3** and diethyldichlorosilane **9**[4,5] in a continuous process (Scheme 2).

The absence of triethylchloro- **11** and tetraethylsilane **12**, which could have been formed from **9** with **8** (Scheme 3), is due to silane **9** ethoxylation with ethoxymagnesium chloride **7** and the reaction of diethyl(ethoxy)chlorosilane **13** with **8** (Scheme 4).

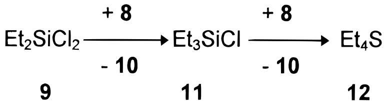
Scheme 1



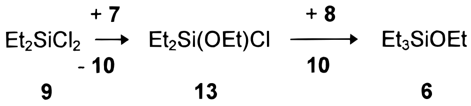
Scheme 2



Scheme 3



Scheme 4



The use of the mixture of ethoxysilane **3** and dichlorosilane **9** for the synthesis of ethylsilanes considerably improved the continuous synthesis: it ensured a higher yield of silane **6** and higher conversion of ethylmagnesium chloride, and also a lower viscosity of the product.

To improve the properties of oligoethylsiloxanes, we proposed the using of a mixture of ethoxysilane **3** and diorganodichlorosilane RR_1SiCl_2 (R = Me, $R_1 = \gamma$-F_3Pr, Cl_2-Ph, C_3H_4S, Ph) in the continuous process.[6−9]

In this work we developed and researched the continuous organomagnesium synthesis of a crude mixture of ethyl-

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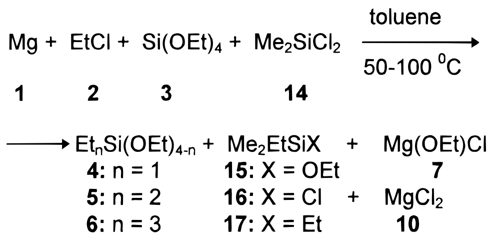
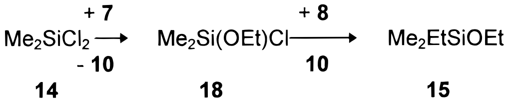
10.1021/op990011g CCC: $19.00

Scheme 5



Scheme 6



ethoxysilanes **4**−**6** and dimethylethylethoxysilane **15** (Scheme 5). We also summarised the results reported previously[10,11] and the recent data.

Ethoxysilane **15** is quantitatively formed by ethoxylation and ethylation of chlorosilane **14** (Scheme 6). Scheme 6 is confirmed experimentally (see Experimental Section).

Results and Discussion

The effect of different parameters on composition of **4**−**6**, **15**−**17**, and conversion of **8** was studied and is discussed in the following sections.

Determination of a Relative Reactivity of 14 and 9.[11] First of all, we evaluated the reactivity of **14** and **9** relative to each other (Scheme 7).

As seen from the test results (Scheme 7; Table 1), products obtained from a mixture of 3.00 M **2**, 1.19 M **3**, 0.25 M **9**, and 0.25 M **14** are ethyl-substituted ethoxysilanes **4**, **5**, **6** (0.124 M), **15** (0.25 M), and dichlorosilane **9** (0.126 M).

The relative contents of **6** and **9** (**6**:**9** = 1:1) and the complete conversion of **14** into **15** show that the reactivity of **14** into **15** is higher by a factor of 2 than the reactivity of **9** into **6**.

Thus, dichlorosilane **14** is well-suited for continuous synthesis of ethyl-substituted ethoxysilanes **4**−**6** and **15**.

The Effect of Concentration of 3 and 14 on the Composition of 4−6 and 15. Then, we studied the influence of the concentrations of the starting reagents **3** and **14** on the composition of the synthesis products (Table 2).

Table 1. **Composition of the mixture of ethyl-substituted silanes and conversion (C) of Grignard reagent 8 during the course of the continuous synthesis**[a]

duration (h)	composition of ethyl-substitued silanes %					C of **8** (%)
	15	**9**	**6**	**5**	**4**	
1	13.8	10.7	7.2	63.0	5.3	89.3
2	13.1	8.1	7.6	67.8	3.4	90.5
3	12.6	8.1	8.9	67.3	3.1	91.5
4	12.9	8.5	8.6	66.3	3.7	91.0
5	13.7	8.4	8.4	65.8	3.7	91.0
6	13.3	7.2	7.4	68.9	3.2	91.1
7	13.1	8.2	8.3	67.5	2.9	91.2

[a] The reaction mixture (Scheme 7) was fed from the supply tank with a dosing pump at a rate of 1100 mL/h. 80 g/h of Mg was loaded at regular intervals (2 times/h).

Table 2. **Effect of reagent concentration on composition of mixture of ethylethoxysilanes and dimethylethylsilanes and conversion (C) of Grignard reagent**[a]

	M		yield (%)[a] for compds listed in Scheme 5							C of **8** (%)
entry	**3**	**14**	**4**	**5**	**6**	**15**	**16**	**17**	**14**	
Type of Granulated Magnesium Is MGP-2 (1.0−1.6 mm)[2,15]										
1	1.36	0.11	8.0	83.8	0.0	8.2	0.0	0.0	0.0	90.7
2	1.32	0.24	7.5	78.5	0.0	13.2	0.0	0.0	0.0	92.3
3	1.26	0.35	7.8	70.2	0.0	22.0	0.0	0.0	0.0	92.0
4	1.19	0.50	7.6	65.6	0.0	26.8	0.0	0.0	0.0	92.3
5	1.07	0.75	1.5	60.8	1.0	25.9	6.8	2.0	2.0	96.3
6	1.20	0.24	0.0	82.2	2.0	15.8	0.0	0.0	0.0	89.0
7	1.15	0.35	0.0	78.0	1.5	20.5	0.0	0.0	0.0	89.0
8	1.09	0.50	0.0	63.5	3.4	25.6	3.0	1.5	3.0	90.7
Type of Milled Magnesium Is MPM-1 (1.0−1.6 mm)[13−15]										
9	1.26	0.29	0.0	81.5	0.5	18.0	0.0	0.0	0.0	94.0
Type of Granulated Magnesium Is L-29 (1.0−2.5 mm)[2,15]										
10	1.26	0.29	6.5	75.3	0.6	17.6	0.0	0.0	0.0	91.0

[a] The weight content of the component is determined from the data of chromatographic analysis. The deviation from the average values did not exceed 0.2% (at content of component up to 20%) and 1.0% in all other cases.

It is clearly seen that an increase in concentration of **14** in the reaction mixture results in increasing of the amount of triorganosilane **15** (entries 1−5) and ethylmagnesium chloride conversion (from 90.7 to 96.3%).

Diethylsilane **5** constitutes the greater part of the composition of the synthesis products (Table 2). The composition of ethylethoxysilanes **4**, **5** (entries 1−4) or **5**, **6** (entries 6−9), or **4**−**6** (entries 5, 10) can be controlled by the concentration of **3** and **14**. Inputing **9** into the mixture of reagents (Scheme 2) was necessary to obtain good yields of **6** (Table 1).

The fact that the reaction products contain practically no tetraethoxysilane and a low amount (0−8%) of ethyltriethoxysilane indicates relatively high rates of reactions (Scheme 1; $n = 1, 2$); a high dichlorosilane **14** content suggests rather low rates of reactions (Scheme 8).

Therefore, under conditions of the single-stage continuous organomagnesium synthesis, the reactivity of ethoxysilanes **3** and **4** (catalysts of ethylmagnesium chloride formation) toward ethylmagnesium chloride is higher than that of dichlorosilane **14**. This effect stems from formation of complexes **8** with **3** and **4**.[12]

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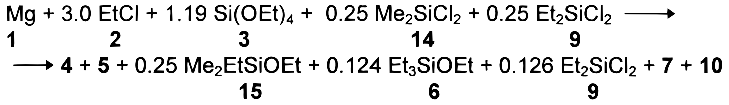
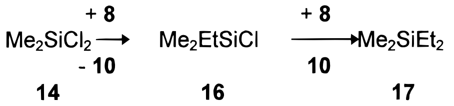
Scheme 7



$$\underset{1}{Mg} + 3.0\,\underset{2}{EtCl} + 1.19\,\underset{3}{Si(OEt)_4} + 0.25\,\underset{14}{Me_2SiCl_2} + 0.25\,\underset{9}{Et_2SiCl_2} \longrightarrow$$

$$\longrightarrow \mathbf{4} + \mathbf{5} + 0.25\,\underset{15}{Me_2EtSiOEt} + 0.124\,\underset{6}{Et_3SiOEt} + 0.126\,\underset{9}{Et_2SiCl_2} + \mathbf{7} + \mathbf{10}$$

Scheme 8



$$\underset{14}{Me_2SiCl_2} \xrightarrow[-\,\mathbf{10}]{+\,\mathbf{8}} \underset{16}{Me_2EtSiCl} \xrightarrow[\mathbf{10}]{+\,\mathbf{8}} \underset{17}{Me_2SiEt_2}$$

Table 3. **Dimethyldichlorosilane conversion in continuous organomagnesium synthesis of ethylethoxysilanes**

M of **14**		Yield (M) of conversion product			amount (%) of **7** consumed in **14** ethoxylation
initial	final	**15**	**16**	**17**	
0.11	0.00	0.11	0.00	0.00	4.2
0.24	0.00	0.24	0.00	0.00	9.5
0.35	0.00	0.35	0.00	0.00	14.5
0.50	0.00	0.50	0.00	0.00	22.0
0.75	0.04	0.53	0.13	0.04	24.8
0.24	0.00	0.24	0.00	0.00	9.9
0.35	0.00	0.35	0.00	0.00	15.1
0.50	0.04	0.38	0.05	0.03	17.0
0.29	0.00	0.29	0.00	0.00	11.5
0.29	0.00	0.29	0.00	0.00	11.9

Table 4. **Content of ethylmagnesium chloride in the product**[a]

duration of synthesis (h)	Content of EtMgCl (%) in expt N								
	1	2	3	4	5	6	7	8	10
2	0.49	0.61	0.37	0.23	0.34	1.24	0.41	0.49	0.22
3	0.29	0.46	0.35	0.34	0.26	1.51	0.31	0.36	0.45
4	0.51	0.67	0.36	0.41	0.43	1.44	0.49	0.43	0.54
5	0.60	0.68	0.35	0.27	0.38	1.12	0.59	0.41	0.50
6	0.69	0.88	0.56	0.30	0.35	1.41	0.73	0.31	0.58

[a] A 0.10% content of ethylmagnesium chloride in the resulting product corresponds to 0.38% of the theoretical amount.

The relative contents of the reaction products (entries 5, 8; Table 2) show that the rates of dichlorosilane **14** ethoxylation and its subsequent conversion to triorganosilane **15** (Scheme 6) are higher by a factor of 3−6 than the rate of its alkylation by **8** (Scheme 8). The quantity of ethoxymagnesium chloride **7** reacted with dichlorosilane **14** increases with increasing content of the latter in the reaction mixture. Note, that although the reaction products contain large amounts of **7** and **14**, not more than 25% of **7** is involved in the reaction (Table 3).

The lack of ethyl chloride **2** in the reaction products and in the gaseous phase in the reactor separator (Table 4) indicates its complete conversion. These data show that among side reactions accompanying Grignard reagent **8** formation, hydrogen abstraction from the solvent molecule is predominant.

Small quantities of **8** (1.6−2.8%) are swept away by the reaction products (Table 5).The yield of Grignard reagent **8** reaches 97.9% (entry 5).

Therefore, the procedure developed in this work allows us to control the composition of the reaction products, and conversion of the initial reagents and intermediates is almost complete.

Effect of Type of Magnesium. Next, we tested a various grades of magnesium. The results (Table 2) show that use of mechanically activated type of magnesium (entry 9) makes it possible to obtain a synthesis product with a high selectivity of the Grignard reagent **8** (and an appreciably lower viscosity in pilot installations). This can apparently be explained by the higher rate of the process of nucleus formation of the Grignard reagent (milled grades of magnesium exhibit a higher activity due to lattice defects), which lowers the size of its particles, increases the rates of their reaction, and changes the size of the particles of the formed magnesium salts **7** and **10**. Similar results were obtained when using tetrachlorosilane[13,14] or phenylmagnesium chloride (in situ).[14−17] The minimum amount of magnesium (0.2−3.5%) is carried away by the synthesis products (Table 6). Thus, granulated and milled types of magnesium are well-suited for continuous synthesis of ethyl-substituted silanes.

In 10 h of continuous operation, the initially loaded magnesium (500 g) is twice replaced completely by magnesium loaded in the course of the reaction. Therefore, the apparatus design and size of magnesium grain (1.0−1.6 mm) provide effective removal of solid products (magnesium salts **7** and **10**, and Grignard reagent **8**) as well as complete (96.5−99.8%) conversion of magnesium.

Effect of Type of Solvent: A Mixture of Toluene with Oligoethylsiloxanes. After that, to reduce the amount of regenerated solvent (toluene), by known procedures,[18,19] we proposed using a continuous process of its mixture with oligoethylsiloxanes (up 20%) modified with dimethylethylsiloxy groups /bp 60−190 °C/1−3 Torr/ (entry 10). It allowed us to decrease the load on the stirrer motor and to stabilize continuous working of the reactor. These effects

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Table 5. **Composition of the gas phase in the separator of the reactor**

compnt	gas content (vol %) in expt N								
	1	2	3	4	5	6	7	8	10
ethylene	7	10−16	3−5	4−5	17	2−5	4−7	4−5	6
ethane	65	51−60	74−81	79−81	46	26−45	54−74	30−44	70
butane	12	15−20	7−9	7−8	17	5−7	11−15	6−12	9
ethyl chloride	0	0.1−0.2	0	0	0	0	0	0	0
toluene	16	10−13	7−15	6−9	20	42−58	12−19	38−56	15

Table 6. **Content of magnesium in the product**[a]

duration of synthesis (h)	Content of Mg (%) in expt N							
	1	2	3	4	5	7	9	10
2	0.01	0.01	0.21	0.04	0.23	0.02	0.24	0.00
3	0.01	0.01	0.15	0.24	0.27	0.02	0.52	0.01
4	0.02	0.02	0.19	0.24	0.25	0.06	0.24	0.01
5	0.05	0.01	0.09	0.15	0.26	0.02	0.53	0.01
6	0.09	0.02	0.04	0.21	0.16	0.01	0.38	0.01

[a] A 0.10% content of magnesium in the resulting product corresponds to 1.37% of the loaded amount.

stem from formation of oligosiloxane complexes with magnesium salts **7** and **10**, and from the lubricating properties of oligoethylsiloxanes.

Thus, the procedure developed in this work allows us to control the composition and properties of the reaction products, which are used in subsequent preparation of modified oligoethylsiloxanes. And conversion of the initial reagents and intermediates is almost complete.

Preparation of Modified Oligoethylsiloxanes. Finally, from the reaction products (without recovery of individual monomers) we recovered for the first time oligoethylsiloxane liquids with the terminal dimethylethylsiloxy groups.

Some properties of oligoethylsiloxanes are presented in Table 7. As can be seen, the properties of these compounds are determined by the content of the terminal triorganosiloxy groups (or by the content of **3** and **14** into the reaction mixture).

From the reaction product (entry 1; Table 2,7), we obtained PES-5 polisiloxane liquid which meets the requirements of the All-Union State Standard (GOST) 13004−77 (viscosity 219 centistoke; flash point 265 °C; pH 6.5; silicon content 27.9%; ethoxy group and moisture contents less than 0.25 and 0.005%, respectively).

From the reaction product (entry 3, Table 2,7), we obtained PES-7 polisiloxane liquid which meets the requirements of the All-Union State Standard (GOST) 5.868−71 (viscosity 45.7 centistoke; flash point >200 °C; pH 6.4; silicon content 27.9%; ethoxy group and moisture contents less than 0.25 and 0.005%, respectively).

It is important to note, that the lubricating properties of these liquids (determined by E. B. Markina /VNII NP/) are significantly better than those of the nonmodified compounds.

For example, the diameter of the wear spot for fraction 7 and 5 (entries 3, 4, 6, and 7)/test conditions: 50 N, 50 °C, 2h/ is 0.35, 0.32, 0.30, and 0.60 mm, respectively, i.e., lower than 0.73 mm in the case of nonmodified fraction 5 prepared from 1.260 mol of tetraethoxysilane and 0.335 mol of diethyldichlorosilane.

Hence, these modified liquids were used as a basis for technical liquid whose compounding and preparation procedure were developed at VNII NP (All-Russia Research Institute of Oil Refining). The main results of this work were patented.[20,21]

Conclusions

We have presented an efficient route for the commercial-scale manufacture of the modified oligoethylsiloxanes with the terminal dimethylethylsiloxy groups, which are characterized by improved lubricating properties. We have developed for the first time and put into operation on a pilot scale the efficient continuous organomagnesium synthesis of ethyl-substituted silanes from the mixture of ethyl chloride, tetraethoxysilane (catalyst of ethylmagnesium chloride (in situ) formation), and dimethyldichlorosilane. We have demonstrated an original method for the direct conversion of dimethyldichlorosilane to dimethylethylethoxysilane (Scheme 6). The granulated and milled (better) types of magnesium are well-suited for continuous synthesis of ethyl-substituted silanes. Conversion of the initial reagents and intermediates is almost complete. We proposed using of mixture of toluene with oligoethylsiloxanes (up 20%) modified dimethylethylsiloxy groups/bp 60−190 °C/1−3 Torr/ in continuous process. It allowed us to decrease the load on the stirrer motor and stabilized continuous working of the reactor. The procedure have developed in this work allows us to control the composition and properties of the reaction products and some properties of modified oligoethylsiloxanes (are determined by the content of **3** and **14** into the reaction mixture).

Experimental Section

General Procedures. All reagents and solvents were obtained from SILANE and used without further purification. The purity of starting magnesium: MGP-2 (96−98%); MPM-1 (>99%); L-29 (96−98%).

The liquid phase obtained in the synthesis was separated by centrifugation and analyzed on an LKhM-80 chromatograph[5] (2 m × 4 mm column, 5% E-301 on Celite 545,

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Table 7. **Properties of oligomer fractions**

entry	fraction N	bp (°C) 1−3 Torr	yield (%)	viscosity at 20 °C (cst)	refractive index at 20 °C	density at 20 °C (g cm^{-3})
1	2	110−150	6.3	9.3	1.4341	0.956
	3	150−185	24.4	13.6	1.4349	0.960
	4	185−250	17.8	36.1	1.4381	0.975
	5	>250	51.5	212.5	1.4485	0.995
2	1	60−110	1.2	[a]	1.4233	0.874
	2	110−150	11.5	11.9	1.4338	0.949
	3	150−185	20.4	12.6	1.4334	0.956
	4	185−250	22.5	28.1	1.4371	0.969
	5	>250	44.4	143.5	1.4433	0.991
3	1	60−110	0.8	4.3	1.4278	0.919
	2	110−150	14.4	6.1	1.4301	0.931
	3	150−190	30.2	12.0	1.4318	0.948
	7	>190	54.6	45.7	1.4378	0.971
4	1	60−110	2.3	3.0	1.4241	0.886
	2	110−150	9.9	4.9	1.4275	0.916
	3	150−190	32.3	10.5	1.4312	0.941
	7	>190	52.5	38.6	1.4371	0.967
5	1	60−110	2.9	2.4	1.4196	0.942
	2	110−150	18.7	4.4	1.4245	0.905
	3	150−190	33.7	9.4	1.4300	0.931
	7	>190	44.7	29.0	1.4358	0.951
6	1	60−110	0.7	2.6	1.4292	0.902
	2	110−150	17.5	5.0	1.4309	0.932
	3	150−190	34.4	10.0	1.4338	0.940
	7	>190	47.4	36.8	1.4402	0.961
7	1	60−110	1.3	2.2	1.4280	0.879
	2	110−150	8.6	3.8	1.4304	0.907
	3	150−190	45.1	9.3	1.4348	0.931
	7	>190	45.0	31.4	1.4412	0.949
8	1	60−110	5.2	2.0	1.4214	0.866
	2	110−150	13.7	4.4	1.4270	0.906
	3	150−190	34.8	9.0	1.4308	0.921
	7	>190	46.0	24.5	[a]	[a]
9	1	60−110	0.7	2.6	1.4251	0.900
	2	110−150	5.1	8.0	1.4326	0.930
	3	150−190	29.5	10.9	1.4336	0.942
	7	>190	64.7	60.4	1.4408	0.963
10	7	>190	63.0	63.5	[a]	[a]

[a] Not measured.

detector temperature 350 °C, vaporizer temperature 350 °C, programmed heating from 50 to 300 °C at a rate of 12 deg min^{-1}, carrier gas helium, flow rate 50 mL min^{-1}, detector current 100 mA).

The content of magnesium in the product was determined from the amount of hydrogen released after the decomposition of the sample (0.3−0.5 g) with 20 mL of sulfuric acid (1:3), using a 2 m × 4 mm column packed with zeolite 5A (0.250−0.315 mm grains) and the calibration curve. Temperatures of the vaporizer, the column, and the detector were 50, 35 and 40 °C, respectively. The carrier gas (argon) flow rate was 60 mL min^{-1}. The detector current was 100 mA. The hydrogen content was determined from the peak height on the 8-mV scale of potentiometer from two parallel findings.

The ethylmagnesium chloride content was determined from the amount of ethane formed after the sample (3.0−9.0 g) decomposition with distilled water (20 mL) using a 2 m × 4 mm column packed with Polysorb-1 and the calibration curve. Temperatures of the vaporizer, the column, and the detector were 50, 35, and 40 °C, respectively. The carrier gas (helium) flow rate was 60 mL min^{-1}. The detector current was 100 mA. The ethane content was determined from the peak area from two parallel findings.

The gaseous phase from the reactor separator was analyzed on an LKhM-8MD chromatograph (2 m × 3 mm column packed with Polysorb-1). The detector and vaporizer temperature was 200 °C; the columns were heated in programmed mode with a 12 deg min^{-1} heating rate over the temperature range from 35 to 200 °C. The carrier gas (helium) flow rate was 30 mL min^{-1}. The detector current was 90 mA.

Control Batch Synthesis of Ethyl-Substituted Silanes. (A) A batch of Mg turnings (27.0 g, 1.111 mol) was charged into a 1-L round-bottom four-necked flask equipped with a mechanical stirrer with a hydroseal, a reflux condenser, a thermometer, and a dropping funnel. Mg was heated to 75 °C and stirred at this temperature for 20 min. To the Mg turnings was quickly added a portion (10−20 mL) of a mixture of **2** (70.0 mL, 1.000 mol), **3** (101.0 mL, 0.455 mol), and toluene (150.0 mL). The reaction self-initiated within 10 min. The remaining solution of **2** and **3** was added (continuous addition) into the flask over 20 min at 55−70 °C; a cooling bath was needed to keep the temperature within this range. When the addition was complete, the mixture was stirred for 2 h at 60 °C and a sample was withdrawn to analyse the reaction products **(a).**

Silane **14** (30.0 mL, 0.250 mol) was added to the above reaction product over a 1 min period at 45 °C, the reaction mixture was further stirred for 1 h at 63 °C, and the sample for analysis was taken **(b)**.

(B) Similar to the procedure of (A) an amount of Mg turnings (40 g, 1.646 mol) was heated to 75 °C and stirred at this temperature for 20 min. To the Mg turnings was quickly added a portion (10−20 mL) of a mixture of **2** (105.0 mL, 1.500 mol), **3** (147.0 mL, 0.660 mol), **14** (30.0 mL, 0.250 mol), and toluene (240.0 mL). The reaction self-initiated within 5 min. The remaining solution of **2**, **3,** and **14** was added (continuous addition) into the flask over 35 min at 60−65 °C; a cooling bath was needed to keep the temperature within this range. When the addition was complete, the mixture was stirred for 2 h at 60 °C, and a sample was withdrawn to analyse the reaction products **(c)**.

(C) The sample of reaction products **(d)** was prepared from **1**, **2**, **3,** and **14** (60.0 mL, 0.500 mol) in a manner similar to that described above (B).

Table 8. **Parameters of continuous organomagnesium synthesis of ethyl-substituted silanes**

exptN	feed rate of the reaction mixture (ml h^{-1})	Temperature in indicated zones of synthesis reactor (°C)					heat removal from the first reaction zone (kcal h^{-1})
		1	2	3	4	separator	
1	1030−1080	80−81	67	65−66	86	82	172
2	1050−1120	79−82	65−68	65−66	85−87	80−82	196−208
3	960−1030	77−83	64−66	63−64	85−86	81−85	162−177
4	1050−1140	80−86	64−65	63−64	86	86	172−184
5	1040−1110	78−83	68	64	86	83	192−194
6	1010−1060	95−98	50−60	48−58	83	76	195−219
7	980−1220	88−95	48−50	48−50	83	74	195−228
8	1150−1220	90−91	58−64	54−59	84−85	75−76	227−248
9	1160−1270	86−92	63−69	55−63	76−78	73−75	222−234
10	1100−1220	84−90	62−74	66−70	77−79	73−75	220−233

Table 9. **Characteristics of intermediate products and parameters of catalic rearrangement (CR) of modified oligoethylsiloxanes (OES)**

expt N	Solution of OES		Solution of MgCl			viscosity of OES[a] (cSt)	parameters of CR	
	OES (%)	*d* (g cm^{-3})	$MgCl_2$ (%)	*d* (g cm^{-3})	HCl (g L^{-1})		τ (h)	*t* (°C)
1	27.9	0.89	19−22	1.14−1.15	20−52	7.9/42.0	12	110−122
2	28.6	0.88	18−22	1.15−1.16	20−38	5.3/24.4	12	90−110
3	28.8	0.88	19−25	1.15−1.16	31−46	4.7/14.7	18	120−130
4	28.7	0.88	19−21	1.15−1.17	22−52	4.6/13.7	18	120−130
5	28.0	0.87	18−22	1.15−1.17	20−43	3.6/9.9	18	120−130
6	23.6	0.87	27−32	1.18−1.20	27−36	4.8/14.4	28	130−140
7	26.4	0.87	22−25	1.16−1.18	42−52	3.6/11.1	26	133−140
8	25.0	0.87	28−32	1.20−1.23	21−31	4.4/9.9	30	140
9	34.3[b]	0.88	28−33	1.18−1.20	30−42	6.5/23.1	22	100−122
10	34.7[c]	0.88	21−26	1.18−1.21	41−57	5.7/24.0	21	107−137

[a]Before CR/after CR. [b] OES were added to the synthesis products. [c] OES were added to the reaction mixture in place of part of toluene.

The results of analysis of **(a−d)** (wt %) show that in our tests ethoxylation of **14** follows Scheme 6.

	(**a**)	(**b**)	(**c**)	(**d**)
$Si(OEt)_4$	1.4	1.0	6.5	15.9
$EtSi(OEt)_3$	21.6	15.7	17.5	11.8
$Et_2Si(OEt)_2$	77.0	56.1	48.1	30.6
Et_3SiOEt	0.0	0.0	0.0	0.0
Me_2SiCl_2	0.0	17.4	0.0	6.8
$Me_2EtSiCl$	0.0	2.2	2.1	6.6
$Me_2EtSiOEt$	0.0	7.6	25.8	26.8
X	0.0	0.0	0.0	1.5
conversion of EtMgCl, %	80.1	82.3	87.6	85.7

Continuous Synthesis. The continuous synthesis was carried out using a column apparatus (Figure 1)[2] divided along the vertical into four zones by jackets. The zones are numbered from the bottom to the top. To initiate the process, we fed into the reactor from a supply tank using a dosing pump 100 mL of toluene. Then 100 g of magnesium was loaded into the reactor through a funnel on the cap of the reactor separator. The contents of the reactor were heated to to 60−70 °C by feeding hot water from a thermostat to the jacket of the first zone and a heat-transfer agent from a another thermostat to the jackets of the fourth zone and the separator. When the temperature of the first zone reached 60 °C, we began introduction of the reaction mixture of a given composition from the supply tank with the dosing pump at a rate 400−600 mL h^{-1}. After an induction period

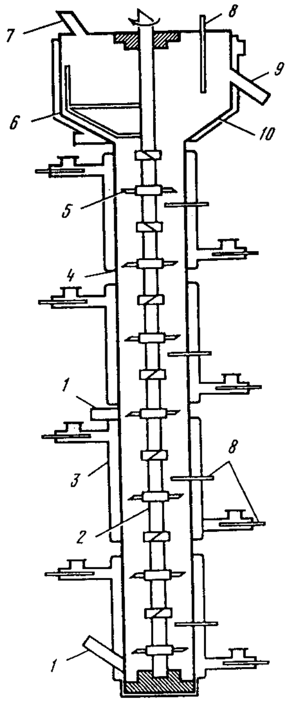

Figure 1. **Synthesis reactor:[2] 1, connecting pipe for mixture input; 2, stirrer; 3, cooling jacket; 4, reactor body; 5, paddle; 6, frame; 7, connecting pipe for magnesium input; 8, thermocouple pocket; 9, connecting pipe for product removal; 10, separator.**

(usually 5−20 min), the temperature into the first zone increased to 80−100 °C, indicating the completion of the induction period and onset of the reaction. The water was fed through the jacket of the first reactor zone for cooling. A heat-transfer agent was fed through the jackets of the fourth zone and the separator from a another thermostat.

Every 5 min, 50 g of magnesium was introduced into the reactor through the funnel, until the total amount in the reactor became 500 g; at this moment, we began to take off the synthesis product from the reactor into the receiver or into the continuous hydrolysis unit.

After that the feeding rate was increased to the prescribed value over a period of 1 h. Simultaneously the prescribed synthesis temperature mode of the process was established by controlling the input rate of the cooling water and the temperature of the heat-transfer agent. The rate of stirrer rotation was maintained at 120−140 rpm. The additional amounts of magnesium (up to the prescribed amount) were loaded at regular intervals (2 times an hour). The mixture moved in the reactor from the bottom to the top through the magnesium bed, reacting with this layer.

The parameters of the continuous synthesis are listed in Table 8. The synthesis product as a suspension of a magnesium salts into ethylethoxysilanes and toluene from the separator was directed into a collector (entries 1−5, 9) or into a setup for continuous hydrolysis (entries 6−8, 10). From the discharge duct, samples were withdrawn every hour to determine the composition of the synthesis product. From the reactor separator, samples were withdrawn every hour to determine the composition of the gaseous phase.

After collecting the required amount of the product, the heating was swiched off, and the reactor was cooled to 40 °C by feeding water into the jackets. Simultaneously, toluene was fed into the reactor (usually 0.5 L). Then the bottom cap was screwed off, and the contents were unloaded into a special vessel.

Safety and hazards associated to the continuous process are typical of the batch process.

Synthesis of Modified Oligosiloxanes. The syntheses were performed according to the procedure given previously.[17,22] The parameters of the catalytic rearrangement (CR) and the characteristics of the intermediates are listed in Table 9.

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